

AD-A144 729

A POTENTIOMETRIC STUDY OF CHLOROALUMINATE EQUILIBRIA IN 1/1  
THE ALUMINUM CHLO. (U) FRANK J SEILER RESEARCH LAB  
UNITED STATES AIR FORCE ACADEMY C. L. HUSSEY ET AL.

UNCLASSIFIED

JUN 84 FJSRL-TR-83-0007

F/G 7/4

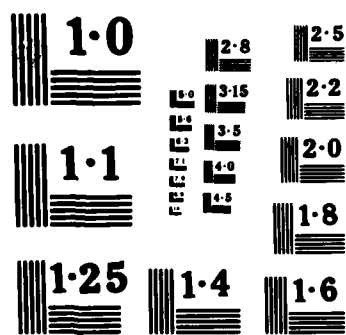
NL

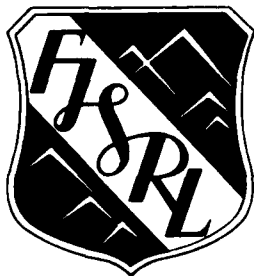


END

FILMED

DTIC





AD-A144 729



DTIC FILE COPY

FRANK J. SEILER RESEARCH LABORATORY

FJSRL-TR-83-0007

JUNE 1984

**A POTENTIOMETRIC STUDY OF  
CHLOROALUMINATE EQUILIBRIA IN THE  
ALUMINUM CHLORIDE - 1-METHYL-2-  
ETHYLIMIDAZOLIUM CHLORIDE  
IONIC LIQUID**

**Charles L. Hussey  
Towner B. Scheffler  
John S. Wilkes  
Armand A. Fannin, Jr.**

AUG 21 1984

A

**PROJECT 2303**

APPROVED FOR PUBLIC RELEASE;  
DISTRIBUTION UNLIMITED.

**AIR FORCE SYSTEMS COMMAND  
UNITED STATES AIR FORCE**

**84 08 21 073**

This document was prepared by the Electrochemistry Division, Directorate of Chemical Sciences, Frank J. Seiler Research Laboratory, United States Air Force Academy, CO. The research was conducted under Project Work Unit number 2303-F2-10. John S. Wilkes was the project scientist.

When U.S. Government drawings, specifications or other data are used for any purpose other than a definitely related government procurement operation, the government thereby incurs no responsibility nor any obligation whatsoever, and the fact that the government may have formulated, furnished or in any way supplied the said drawings, specifications or other data is not to be regarded by implication or otherwise, as in any manner licensing the holder or any other person or corporation or conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto.

Inquiries concerning the technical content of this document should be addressed to the Frank J. Seiler Research Laboratory (AFSC), FJSRL/MC, USAF Academy, CO 80840. Phone AC 303 472-2655.

This report has been reviewed by the Commander and is releasable to the National Technical Information Service (NTIS). At NTIS it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.



John S. Wilkes  
Project Scientist



Chester J. Dymek, Jr., Lt Col  
Director, Chemical Sciences



Kenneth E. Siegenthaler, Lt Col  
Chief Scientist

Copies of this report should not be returned unless return is required by security considerations, contractual obligations, or notice on a specific document.

Printed in the United States of America. Qualified requestors may obtain additional copies from the Defense Documentation Center. All others should apply to:

National Technical Information Service  
6285 Port Royal Road  
Springfield, Virginia 22161

## REPORT DOCUMENTATION PAGE ADA

1a. REPORT SECURITY CLASSIFICATION <b>Unclassified</b>		1b. RESTRICTIVE MARKINGS	
2a. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION/AVAILABILITY OF REPORT  Approved for public release; distribution unlimited.	
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE		4. PERFORMING ORGANIZATION REPORT NUMBER(S)  FJSRL-TR-83-0007	
5. MONITORING ORGANIZATION REPORT NUMBER(S)		6a. NAME OF PERFORMING ORGANIZATION <b>Frank J. Seiler Research Laboratory</b>	
6b. OFFICE SYMBOL (If applicable) <b>FJSRL/NC</b>		7a. NAME OF MONITORING ORGANIZATION	
6c. ADDRESS (City, State and ZIP Code) <b>USAF Academy Colorado Springs CO 80840</b>		7b. ADDRESS (City, State and ZIP Code)	
8a. NAME OF FUNDING/SPONSORING ORGANIZATION <b>AF Office of Scientific Research</b>		8b. OFFICE SYMBOL (If applicable) <b>AFOSR</b>	
9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER		10. SOURCE OF FUNDING NOS.	
8c. ADDRESS (City, State and ZIP Code) <b>Bldg. 410 Bolling AFB DC 20332</b>		PROGRAM ELEMENT NO.  6.1	PROJECT NO.  2303
		TASK NO.  F2	WORK UNIT NO.  10
11. TITLE (Include Security Classification) <b>A Potentiometric Study of Chloroaluminate Equilibria in the Aluminum Chloride-1-methyl-2-ethylimidazolium Chloride</b>			
12. PERSONAL AUTHOR(S) <b>Charles L. Hussey, Towner B. Scheffler, John S. Wilkes, Armand A. Fannin, Jr.</b>			
13a. TYPE OF REPORT <b>interim</b>	13b. TIME COVERED <b>FROM 1 Jul 82 TO 30 Jun 83</b>	14. DATE OF REPORT (Yr., Mo., Day) <b>84/06/16</b>	15. PAGE COUNT <b>18</b>
16. SUPPLEMENTARY NOTATION			
17. COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD <b>07</b>	GROUP <b>04</b>	SUB. GR. <b>chloroaluminate equilibria molten salt</b>	
19. ABSTRACT (Continue on reverse if necessary and identify by block number)			
<p>The upper limit on the stoichiometric equilibrium constant for the tetrachloroaluminate dissociation reaction, <math>\text{SRAI}\text{Cl}_4 \rightleftharpoons \text{RAI}_2\text{Cl}_7 + \text{RCl}</math>, was investigated in the room temperature ionic liquid aluminum chloride-1-methyl-3-ethylimidazolium chloride by means of a potentiometric titration procedure. The values obtained at 40, 50, and 60°C were <math>5.1 \pm 1.4 \times 10^{-17}</math>, <math>1.8 \pm 1.6 \times 10^{-16}</math>, and <math>3.8 \pm 1.1 \times 10^{-16}</math>, respectively. A curve fitting procedure for locating the equivalence point in these titrations is also described.</p>			
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <b>UNCLASSIFIED/UNLIMITED <input checked="" type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS <input type="checkbox"/></b>		21. ABSTRACT SECURITY CLASSIFICATION <b>Unclassified</b>	
22a. NAME OF RESPONSIBLE INDIVIDUAL <b>JOHN S. WILKES</b>		22b. TELEPHONE NUMBER (Include Area Code) <b>(303) 472-2655</b>	22c. OFFICE SYMBOL <b>FJSRL/NC</b>

A Potentiometric Study of Chloroaluminate Equilibria in the  
Aluminum Chloride-1-Methyl-2-Ethylimidazolium  
Chloride Ionic Liquid

Capt. Charles L. Hussey  
Dr. Towner B. Scheffler  
Dr. John S. Wilkes  
Lt. Col. Armand A. Fannin, Jr.

June 1984



A1

Approved for public release; distribution unlimited

Directorate of Chemical Sciences  
The Frank J. Seiler Research Laboratory  
Air Force Systems Command  
United States Air Force Academy  
Colorado Springs, Colorado 80840

## TABLE OF CONTENTS

Table of Contents.....	i
Summary.....	ii
Preface.....	iii
List of Figures.....	iv
List of Tables.....	iv
I. Introduction.....	1
II. Experimental.....	2
III. Results and Discussion.....	3
IV. Conclusion.....	11
V. List of References.....	12
VI. Appendix A.....	13
VII. Appendix B.....	16
VIII. Glossary.....	18

## SUMMARY

→ The upper limit on the stoichiometric equilibrium constant for the tetrachloroaluminate dissociation reaction,  $2\text{RAlCl}_4 \rightleftharpoons \text{RAl}_2\text{Cl}_7 + \text{RCl}$ , was investigated in the room temperature ionic liquid aluminum chloride-1-methyl-3-ethylimidazolium chloride by means of a potentiometric titration procedure.

2 The values obtained at 40, 50, and 60°C were  $5.1 \pm 1.4 \times 10^{-17}$ ,  $1.8 \pm 1.6 \times 10^{-16}$ , and  $3.8 \pm 1.1 \times 10^{-16}$ , respectively. A curve fitting procedure for locating the equivalence point in these titrations is also described.



## PREFACE

This report describes work performed under FJSRL Work Unit 2303-F2-10, Organic and Inorganic Electrochemical Measurements. Portions of the experimental part of this study were carried out in the Department of Chemistry at the University of Mississippi. Capt. Hussey is a reservist assigned to the Air Force Office of Scientific Research and attached to FJSRL. Dr. Scheffler is a National Research Council research associate at FJSRL. Dr. Wilkes and Lt. Col. Fannin are permanent staff members at FJSRL.

### LIST OF FIGURES

Figure 1. Cyclic voltammogram for the reduction of 1-(n-butyl)pyridinium cation at a glassy carbon electrode in 44 mole/o  $\text{AlCl}_3$ -MEIC melt at 40.0°C.

Figure 2. Potentiometric titration curves for the  $\text{AlCl}_3$ -MEIC system.

Figure 3. Distribution of species in the  $\text{AlCl}_3$ -MEIC melt at 40.0°C.

### LIST OF TABLES

Table I. Chloroaluminate autosolvolytic equilibrium constants.

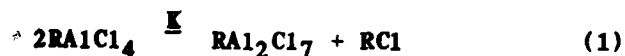
Table A-I. Results for calculation of initial melt compositions.

Table B-I. Example of a fitting cycle for determination of  $\underline{K}'$  from Eq. (B-1).

## I. Introduction

Aluminum chloride can be combined with certain organic salts to produce ionic liquids that are molten at room temperature. Familiar examples of such liquids are mixtures of aluminum chloride with N-(n-butyl)pyridinium chloride (BPC) (1,2). However, a new class of room temperature chloroaluminate melts, based on dialkylimidazolium chloride salts, was described recently (3). Mixtures of aluminum chloride, with one of these salts, 1-methyl-3-ethylimidazolium chloride (MEIC), exhibit both a wider electrochemical window and higher electrical conductivity, and are liquid over a larger composition range than corresponding systems based on N-alkylpyridinium halides.

The Lewis acid-base properties of room temperature chloroaluminate melts are governed essentially by the single equilibrium (3-5):



Melts that contain a molar excess of aluminum chloride to organic salt are Lewis acidic by virtue of the coordinately unsaturated  $\text{Al}_2\text{Cl}_7^-$  ion. Conversely, mixtures that contain an excess of the organic salt relative to aluminum chloride are Lewis basic due to uncomplexed chloride ion.

The acid-base properties of ionic liquids based on  $\text{AlCl}_3$ -BPC have been investigated and estimates of the upper limit on the equilibrium constant for Eq. (1) are available for this liquid (4,5). Karpinski and Osteryoung (6) have demonstrated that it is not possible to measure an exact value of  $K$  for Eq. (1) if aluminum electrodes are used for the measurements. This is because an aluminum electrode immersed in basic melt experiences a mixed potential that is

less negative than the true potential of the Al(III)/Al redox couple. Two sources of this mixed potential have been advanced (6): corrosion of aluminum by the organic cation (this phenomenon is well-known in the  $\text{AlCl}_3$ -BPC melt (7)) and corrosion of aluminum by adventitious hydrogen ion. In place of aluminum electrodes, Karpinski and Osteryoung suggested the use of the  $\text{Cl}_2/\text{Cl}^-$  couple for determining chloride ion activity. Unfortunately, it has been found that  $\text{Cl}_2$  reacts with the organic cation in  $\text{AlCl}_3$ -MEIC melts, eventually chlorinating all available sites on the cation (8). Thus, the chlorine electrode is not the catholicon for these measurements, either.

This technical report describes a study of the acid-base properties of the  $\text{AlCl}_3$ -MEIC melt. Potentiometric measurements were undertaken at aluminum electrodes in order to estimate the upper limit on  $K$  for Eq. (1).

## II. Experimental

Instrumentation. Experiments were conducted in a dry, oxygen-free nitrogen atmosphere inside a Kewaunee Scientific Engineering Corp. dry box system equipped with a Model 2C2500 30-cfm inert-gas purifier. The procedure for estimating the moisture and oxygen content of this dry box using a 25 W light bulb has been described (9). Instrumentation used to perform cyclic voltammetry and to make potentiometric measurements was identical to that used previously (10). Pulse polarographic experiments were undertaken with a PARC Model 174 polarographic analyzer.

Cells and Electrodes. The cell and furnace used were described previously (9). Aluminum electrodes were fashioned from 1.0-mm diameter aluminum wire (Alfa Products, m5N purity). These electrodes were immersed briefly in a

aqueous solution that was 5% (v/v) in HF and 15% (v/v) in  $\text{HNO}_3$ , rinsed with distilled water, and dried under vacuum before use.

Chemicals. Aluminum chloride (Fluka, A.G.) was triply sublimed under vacuum inside the dry box. The synthesis and purification of 1-methyl-3-ethylimidazolium chloride was identical to that described by Wilkes et al. This salt was carefully purified using airless techniques; it was recrystallized three times from mixtures of acetonitrile and ethyl acetate. The oxide content of the  $\text{AlCl}_3$ -MEIC melt was determined with  $\text{TiCl}_4$  using a pulse polarographic method (11). Melts that contained more than 5 ppm oxide were discarded.

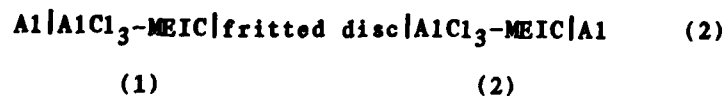
When  $\text{AlCl}_3$  is mixed with MEIC, a violent exothermic reaction takes place which results in sublimation loss of  $\text{AlCl}_3$  and decomposition of small amounts of MEIC. Consequently, it is very difficult to prepare a large amount of melt of an accurately known composition by combining preweighted quantities of the components. Therefore, it was necessary to determine the initial melt composition directly from titration data. Two procedures were used. The first was based on an approximation of Grans method and is similar to that described by Schoebrechts and Gilbert (5). The second method is described in Appendix A. For brevity,  $\text{AlCl}_3$ -MEIC melt compositions specified in this paper are given in terms of the formal mole fraction,  $N$ , or mole percent, mole/o, of  $\text{AlCl}_3$  in the mixture.

### III. Results and Discussion

Stability of aluminum in basic  $\text{AlCl}_3$ -MEIC melt. As previously noted, the instability of aluminum in basic melt can complicate the study of chloroaluminate equilibria. For example, aluminum behaves as a reducing agent

toward the 1-(n-butyl)pyridinium cation in basic  $\text{AlCl}_3$ -BPC melt. The addition of aluminum to this melt produces the highly colored 4,4'-dibutyl-1,1'-bipyridinium monocation radical (9). MNDO calculations suggest that the 1-methyl-3-ethylimidazolium cation is substantially more difficult to reduce than the 1-(n-butyl)pyridinium cation (3). In fact, the latter species can be electrochemically reduced in basic  $\text{AlCl}_3$ -MEIC melt prior to the negative limit of the solvent. Figure 1 shows a cyclic voltammogram for the reduction of 1-(n-butyl)pyridinium cation at a glassy carbon electrode in basic  $\text{AlCl}_3$ -MEIC. The reduction peak potential for this solute, -1.43 V versus aluminum in 66.7 mole/o  $\text{AlCl}_3$ -MEIC, is considerably positive of the negative limit of the 44.4 mole/o  $\text{AlCl}_3$ -MEIC melt at -2.20 V. Thus, aluminum should be more stable thermodynamically with regard to oxidation in basic  $\text{AlCl}_3$ -MEIC relative to basic  $\text{AlCl}_3$ -BPC. Immersion of small pieces of aluminum foil in basic  $\text{AlCl}_3$ -MEIC for several weeks did not result in discernable changes in the aluminum or the melt, while similar experiments with basic  $\text{AlCl}_3$ -BPC indicated reduction of the 1-(n-butyl)pyridinium cation within a few days. However, it was not possible to electrochemically deposit aluminum at aluminum or glassy carbon electrodes in basic  $\text{AlCl}_3$ -MEIC melt; prolonged electrolysis produced an orange-colored solution in the cathode compartment of the cell.

Potentiometric titration experiments. The concentration cell with transference shown below was used to study chloroaluminate equilibria in  $\text{AlCl}_3$ -MEIC melt:



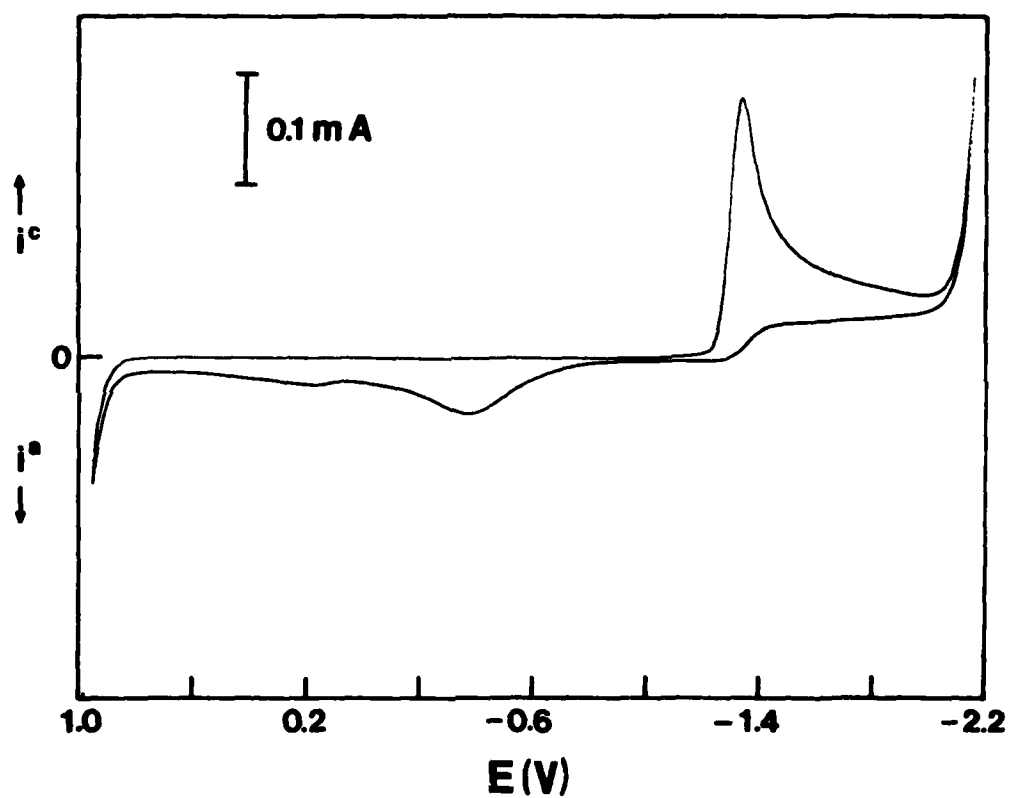


Figure 1. Cyclic voltammogram for the reduction of the 1-(*n*-butyl)pyridinium cation at a glassy electrode in 44 mole/o  $\text{AlCl}_3$ -MBIC melt at  $40.0^\circ\text{C}$ . Sweep rate was 50 mV/sec.

Both compartments of this cell were filled with melt that was ca. 60 mole/o in  $\text{AlCl}_3$  prior to the start of an experiment. Weighed portions of MEIC were added to compartment 2 of the cell during an experiment and the potential of the cell was recorded after dissolution of the MEIC. The aluminum electrodes were carefully wiped with abrasive tissue (Kimwipes) before each data point was recorded. The melt composition in the left-hand cell compartment was kept constant. Figure 2 shows representative titration curves obtained at 40.0, 50.0, and 60.0°C, using this cell. Several experiments were conducted at each temperature. Cell potentials were stable and reproducible throughout each titration experiment.

Analysis of chloroaluminate concentration cells. Øye and King (12) reported that the potential of a chloroaluminate concentration cell with transference, similar to that shown in Eq. (2), is given formally by the expression

$$\underline{FE} = \int_1^2 \frac{1}{3} d\mu_{\text{AlCl}_3} - \frac{t_{\text{Al}}}{3} d\mu_{\text{AlCl}_3} - t_{\text{R}} d\mu_{\text{RCl}} \quad (3)$$

In Eq. (3), RCl represents MEIC, and  $t_{\text{Al}}$  and  $t_{\text{R}}$  are the formal transport numbers of the aluminum ion and the melt cation, respectively. Hussey and Øye (13) have measured transport numbers in the  $\text{AlCl}_3$ -MEIC melt. The internal transport number of the organic cation relative to chloride is 1.00 in this melt. In this event Eq. (3) simplifies to

$$\underline{FE} = \int_1^2 \frac{1}{3} d\mu_{\text{AlCl}_3} - d\mu_{\text{RCl}} \quad (4)$$

Equation (4) may also be written in terms of the activities of the major chloroaluminate species in basic melt



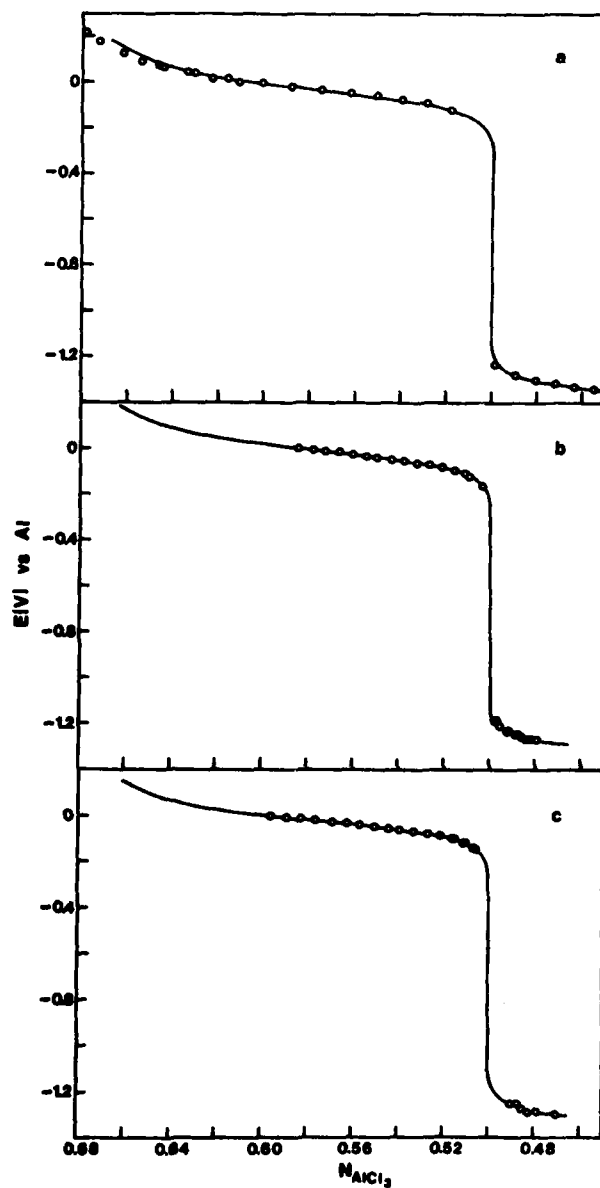


Figure 2. Potentiometric titration curves for the  $\text{AlCl}_3$ -MEIC system; a) 60.0°C, b) 50.0°C, and c) 40.0°C. Solid lines were calculated from the estimated equilibrium constants for Eq. (1) that were determined from the experimental data in each figure.

$$\underline{E} = \frac{RT}{3F} \int_1^2 d \ln a_{\text{RA1Cl}_4} - 4 d \ln a_{\text{RC1}} \quad (5)$$

or in acidic melt

$$\underline{E} = \frac{RT}{3F} \int_1^2 4 d \ln a_{\text{RA1}_2\text{Cl}_7} - 7 d \ln a_{\text{RA1Cl}_4} \quad (6)$$

Autosolvolytic equilibrium constant. - The stoichiometric equilibrium constant for the reaction depicted in Eq. (1) is defined as

$$\underline{K}' = \frac{(\underline{X}_{\text{RC1}})(\underline{X}_{\text{RA1}_2\text{Cl}_7})}{(\underline{X}_{\text{RA1Cl}_4})^2} \quad (7)$$

where  $\underline{X}_{\text{RC1}}$ ,  $\underline{X}_{\text{RA1Cl}_4}$ , and  $\underline{X}_{\text{RA1}_2\text{Cl}_7}$  represent the mole fractions of RC1, RA1Cl<sub>4</sub>, and RA1<sub>2</sub>Cl<sub>7</sub>. Values of  $\underline{K}'$  for the AlCl<sub>3</sub>-MEIC system were obtained by curve fitting data in the vicinity of the 50 mole/o composition to the equation

$$\underline{E} = \frac{4RT}{3F} \ln \frac{\underline{K}'(\underline{X}_{\text{RA1Cl}_4})^2_A}{(\underline{X}_{\text{RC1}})_B(\underline{X}_{\text{RA1}_2\text{Cl}_7})_A} + \frac{RT}{3F} \ln \frac{(\underline{X}_{\text{RA1Cl}_4})_B}{(\underline{X}_{\text{RA1Cl}_4})_A} \quad (8a)$$

where A and B denote acidic and basic compartments, and  $\underline{E} = \underline{E}_B - \underline{E}_A$ . The details of this procedure are given in Appendix B. Average values of the upper limit of  $\underline{K}'$ , resulting from several experiments, are listed in Table I and are compared with other chloroaluminate systems. The approximate distribution of ionic species in AlCl<sub>3</sub>-MEIC melt, calculated by using the  $\underline{K}'$  value at 40°C given in Table I, is shown in Figure 3. The equilibrium constants for Eq. (1) are several orders of magnitude smaller in AlCl<sub>3</sub>-MEIC than those determined for the AlCl<sub>3</sub>-BPC system. This suggests that the value of  $\underline{K}'$  obtained in the present study is probably much closer to the true value of  $\underline{K}'$  than estimates propounded by other workers (4,5). In fact, Karpinski and Osteryoung (6) predict that the

Table I. Chloroaluminate autosolvolysis equilibrium constants.

Melt System	t(°C)	$K'$	ref.
$AlCl_3$ - MEIC	40.0	$(5.1 \pm 1.4^a) \times 10^{-17}$	this work
$AlCl_3$ - MEIC	50.0	$(1.8 \pm 1.6^a) \times 10^{-16}$	this work
$AlCl_3$ - MEIC	60.0	$(3.8 \pm 1.1^a) \times 10^{-16}$	this work
$AlCl_3$ - BPC	40.0	$(1.2 \pm 0.2) \times 10^{-13}$	(5)
$AlCl_3$ - BPC	49.0	$(4.5 \pm 0.4) \times 10^{-13}$	(5)
$AlCl_3$ - BPC	60.0	$1.5 \times 10^{-12}$	(5)
$AlCl_3$ - BDMAPC <sup>b</sup>	40.0	$(8.4 \pm 0.2) \times 10^{-11}$	(14)
$AlCl_3$ - NaCl	175.0	$(1.06 \pm 0.02) \times 10^{-7}$	(15)
$AlCl_3$ - LiCl	175.0	$5 \times 10^{-5}$	(16)
$AlCl_3$ - LiCl	400.0	$1.6 \times 10^{-4}$	(16)
$AlCl_3$ - NaCl	400.00	$1.0 \times 10^{-5}$	(16)
$AlCl_3$ - KCl	400.00	$1.6 \times 10^{-6}$	(16)
$AlCl_3$ - CsCl	400.00	$4.0 \times 10^{-8}$	(16)

<sup>a</sup>95% confidence interval

<sup>b</sup>1-n-butyl-4-(dimethylamino)pyridinium chloride

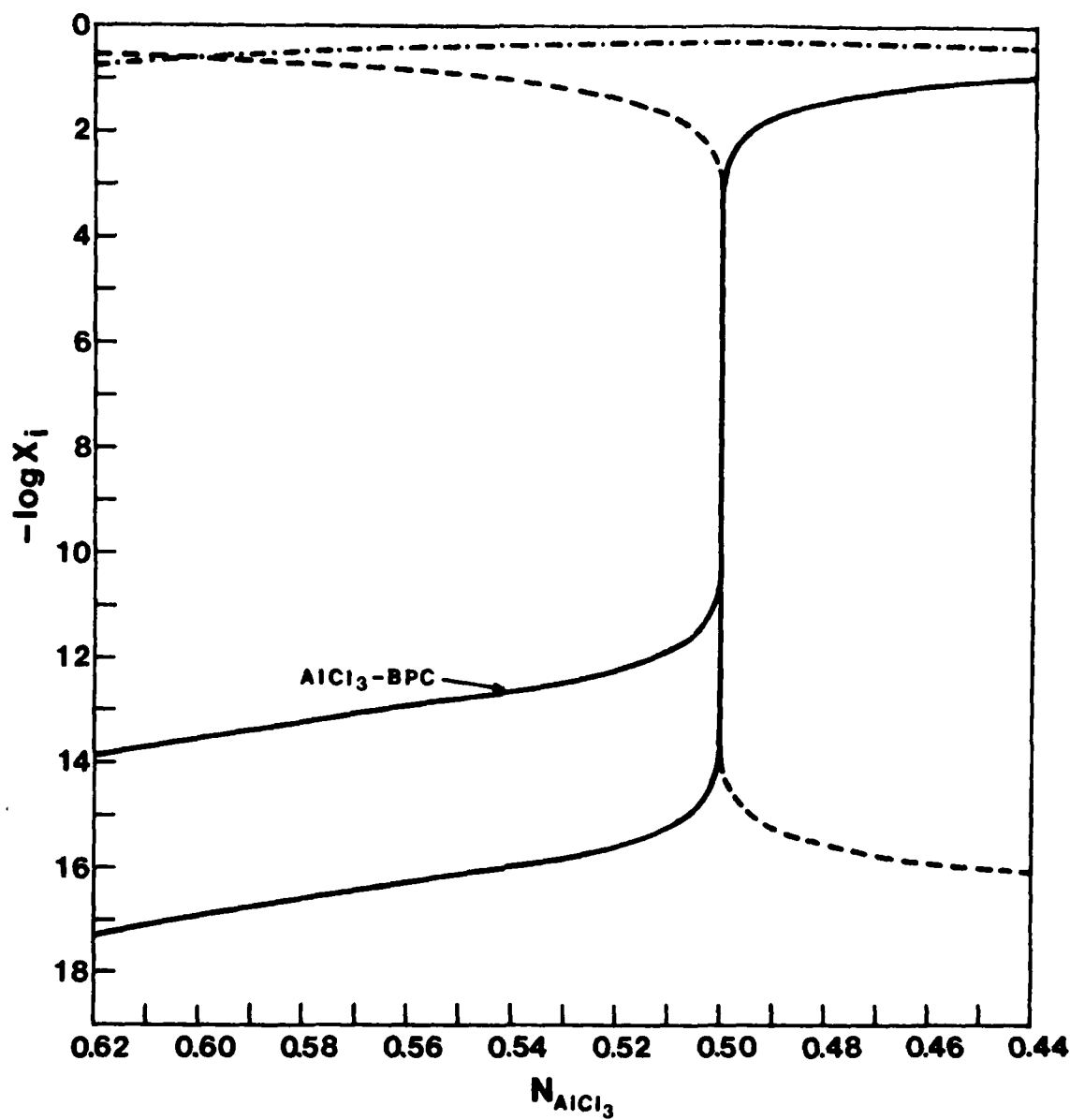


Figure 3. Distribution of species in the  $\text{AlCl}_3$ -NEIC melt at  $40.0^\circ\text{C}$ . —,  $\log X_{\text{RCl}}$ ; - · -,  $\log X_{\text{RA1Cl}_4}$ ; - -,  $\log X_{\text{RA1Cl}_7}$ . The upper limit on  $\log X_{\text{RCl}}$ , attainable in the  $\text{AlCl}_3$ -BPC melt, is shown for comparison. Values of  $\log X_{\text{RCl}}$  for the  $\text{AlCl}_3$ -BPC system were calculated from the estimates of  $\underline{K}$  given in reference 5.

actual value of  $\underline{K'}$  for both the  $\text{AlCl}_3$ -BPC and  $\text{AlCl}_3$ -MEIC melts may lie in the interval from  $10^{-19}$  to  $10^{-15}$ . Nevertheless, the estimates of  $\underline{K'}$  reported herein should be considered to be the upper limit on  $\underline{K'}$  due to the various side reactions which complicate the aluminum electrode reaction in basic melt.

#### IV. Conclusion

The solid lines that appear in Fig. 1 were calculated by using estimates of  $\underline{K'}$  that were determined directly from the experimental data shown in each figure. These lines were calculated by using the integrated forms of Eqs. (5) and (6). It is interesting to note that in every case (Fig. 1) these calculated lines represent the experimental data precisely, except in very acid melt where the  $\text{AlCl}_3$  content exceeds ca. 63 mole/o. It should be noted that recent  $^{27}\text{Al}$  NMR studies suggest the presence of  $\text{Al}_3\text{Cl}_{10}^-$  in very acid  $\text{AlCl}_3$ -MEIC melt (17). Therefore, it may be necessary to consider other equilibria in addition to Eq. (1) in very acidic melt.

## V. List of References

1. H. L. Chum and R. A. Osteryoung in "Ionic Liquids", D. Inman and D. G. Lovering, Eds., Plenum Publishing Co., New York, NY, 1981, Chapter 19.
2. C. L. Hussey in "Advances in Molten Salt Chemistry", Vol. 5, G. Mamantov, Ed., Elsevier Publishing Co., New York, NY, 1983, pp. 185-230.
3. J. S. Wilkes, J. A. Levisky, R. A. Wilson, and C. L. Hussey, Inorg. Chem., **21**, 1263 (1982).
4. R. J. Gale and R. A. Osteryoung, ibid., **18**, 1603 (1979).
5. J. P. Schoebrechts and B. P. Gilbert, J. Electrochem. Soc., **128**, 2679 (1981).
6. Z. J. Karpinski and R. A. Osteryoung, Inorg. Chem., **23**, 1491 (1984).
7. R. J. Gale and R. A. Osteryoung, J. Electrochem. Soc., **127**, 2167 (1980).
8. J. S. Wilkes, unpublished data.
9. T. M. Laher and C. L. Hussey, Inorg. Chem., **21**, 4079 (1982).
10. C. L. Hussey and T. M. Laher, ibid., **20**, 4201 (1981).
11. Z. Stojek, H. Ling, and R. A. Osteryoung, J. Electroanal. Chem., **119**, 365 (1981).
12. H. A. Øye and L. A. King, Inorg. Nucl. Chem. Lett., **16**, 547 (1980).
13. C. L. Hussey and H. A. Øye, J. Electrochem. Soc., **131**, 1621 (1984).
14. G. T. Cheek and R. A. Osteryoung, Inorg. Chem., **21**, 3581 (1982).
15. L. G. Boxall, H. L. Jones, and R. A. Osteryoung, J. Electrochem. Soc., **120**, 223 (1973).
16. G. Torsi and G. Mamantov, Inorg. Chem., **11**, 1439 (1972).
17. J. S. Wilkes, unpublished data.

# VI. Appendix A:

The initial composition of the melt in the cell (Eq. (2)) and each new composition arising in compartment 2 of the cell after the addition of a known amount of MEIC were determined by the curve fitting technique described below. When  $\text{RAI}_2\text{Cl}_7$  and  $\text{RAICl}_4$  in the equation

$$E = \frac{4RT}{3F} \ln \frac{(\bar{x}_{\text{RAI}_2\text{Cl}_7})_2}{(\bar{x}_{\text{RAI}_2\text{Cl}_7})_1} + \frac{7RT}{3F} \ln \frac{(\bar{x}_{\text{RAICl}_4})_1}{(\bar{x}_{\text{RAICl}_4})_2} \quad (\text{A-1})$$

are represented in terms of the apparent mole fractions of  $\text{AlCl}_3$  in compartments 1 and 2 of the cell  $N_1$  and  $N_2$ , respectively, Eq. (A-2) results:

$$E = \frac{4RT}{3F} \ln \left[ \frac{2N_2-1}{2N_1-1} \right] \left[ \frac{1-N_2}{1-N_1} \right] + \frac{7RT}{3F} \ln \left[ \frac{2-3N_1}{2-3N_2} \right] \left[ \frac{1-N_2}{1-N_1} \right] \quad (\text{A-2})$$

Furthermore,  $N_1$  and  $N_2$  can be expressed in terms of the initial weight of melt,  $\bar{W}_m$ , and the initial weight of salt,  $\bar{W}_s^i$ , and the cumulative weight of salt added at each point,  $\bar{W}_s$ , in compartment 2, according to Eqs. (A-3) and (A-4):

$$N_1 = \frac{\bar{W}_m - \bar{W}_s^i}{\bar{W}_m - \bar{W}_s^i(1-R)} \quad (\text{A-3})$$

$$N_2 = \frac{\bar{W}_m - \bar{W}_s^i}{\bar{W}_m - \bar{W}_s^i(1-R) + \bar{W}_s R} \quad (\text{A-4})$$

$R$  represents the ratio of the formula weight of  $\text{AlCl}_3$  to that of the organic salt. Substitution of Eqs. (A-3) and (A-4) into (A-2) results in a complex equation that can be computer fitted to measurements of  $E$  at each  $\bar{W}_s$  in acidic melt. This equation can be used to calculate  $\bar{W}_s^i$  if  $\bar{W}_m$  is known.

A Fortran IV computer program was written for this purpose. This program uses a Taylor series linearized least-squares routine to obtain the value of  $\bar{W}_2^i$  that minimized the error between the experimental potential and the calculated potential. Estimates of the melt composition obtained with this procedure are at least as good as those obtained by using Grans method (5), cf., Table A-I. One significant advantage of the procedure described herein over the other method (5) is that it is not necessary to collect a large amount of titration data immediately prior to the equivalence point. This can result in considerable experimental convenience when a good estimate of the initial melt composition is not available.



Table A-I. Results for calculation of initial melt compositions.

t (°C)	Initial melt composition (mole/o $\text{AlCl}_3$ )		% relative difference
	this work	Grans method (5)	
40.0	60.73	60.10	1.0
	60.34	59.72	1.0
	59.54	59.45	0.2
50.0	58.83	58.59	0.4
	58.43	58.27	0.3
60.0	60.30	59.45	1.4
	61.07	59.83	2.1
	59.08	59.09	0.0
	59.82	60.16	-0.6

VII. Appendix B:

The values of  $\underline{K}'$  that appear in Table I were calculated from potentiometric titration data in the  $50.0 \pm 4.0$  mole/o composition region using this modified version of Eq. (8):

$$\underline{E}_i - \underline{E}_j = \frac{4RT}{3F} \ln \frac{(2-3\underline{N}_i)^2(1-\underline{N}_i) \underline{K}'}{(1-\underline{N}_i)(2\underline{N}_i-1)(1-2\underline{N}_j)} + \frac{RT}{3F} \ln \frac{\underline{N}_i(1-\underline{N}_i)}{(1-\underline{N}_j)(2-3\underline{N}_i)} \quad (B-1)$$

Data, consisting of the potential differences between an acidic reference point,  $\underline{N}_i$ , and a series of basic data points,  $\underline{N}_j$ , were fitted to Eq. (B-1) so as to minimize the sum of the errors between calculated and experimental values of  $\underline{E}_i - \underline{E}_j$ . This procedure was repeated successively for each value of  $\underline{N}_i$  that was in the appropriate composition range of the data set. Values of  $\underline{K}'$  obtained during each cycle were then averaged to give the best estimate of  $\underline{K}'$  for the experiment. A sample of the output obtained during a fitting cycle with the Fortran IV computer program written for this purpose is shown in Table B-I.

Table B-I. Example of a fitting cycle for determination of  $\underline{K}'$  from Eq. (B-1).

$\underline{E}_i - \underline{E}_j$ (V)		Error(V)	$\underline{N}_j$
exptl.	calcd.		
-1.1198	-1.1587	$3.89 \times 10^{-2}$	0.4946
-1.1826	-1.1807	$-1.91 \times 10^{-3}$	0.4900
-1.1816	-1.1898	$8.15 \times 10^{-3}$	0.4871
-1.2038	-1.1953	$-8.46 \times 10^{-3}$	0.4849
-1.2203	-1.2002	$-2.01 \times 10^{-2}$	0.4827
-1.2183	-1.2077	$-1.06 \times 10^{-2}$	0.4786
-1.2286	-1.2194	$-9.16 \times 10^{-3}$	0.4701

temperature = 40.0°C

$\underline{E}_1 = -0.0751$  V

$\underline{N}_1 = 0.5265$

$\underline{K}' = 3.8 \times 10^{-17}$

Standard deviation of the fit =  $1.34 \times 10^{-3}$ (V)

Convergence occurred in 8 iterations

Cycle no. = 2

VIII. Glossary:

- $a_i$  activity of component i, Eqs. (5) and (6).
- $E$  cell potential (V).
- $E_1$  cell potential (V), acid melt in compartment 2, Eq. (2).
- $E_j$  cell potential (V), basic melt in compartment 2, Eq. (2).
- $K'$  stoichiometric equilibrium constant, Eq. (1).
- $N$  mole fraction of  $AlCl_3$ .
- $N_1$  mole fraction of  $AlCl_3$  in acidic melt.
- $N_j$  mole fraction of  $AlCl_3$  in basic melt.
- $N_1$  mole fraction of  $AlCl_3$  in compartment 1, Eq. (2).
- $N_2$  mole fraction of  $AlCl_3$  in compartment 2, Eq. (2).
- $t_i$  transport number.
- $X_1$  mole fraction.
- $W_m$  initial weight of melt (g).
- $W_s$  cumulative weight of MEIC added (g).
- $W_s^i$  initial weight of MEIC in melt (g).
- $\mu_i$  chemical potential.

